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Durability of Lime Carbonates in Soils

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DURABILITY OF LIME CARBONATES IN SOILS

BY

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B. S. University of Utah, 1910

THESIS

Submitted in Partial Fulfillment of the Requirements for the

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THE GRADUATE SCHOOL

May 31, 1913

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

WALLACE MACFARLANE

ENTITLED DURABILITY OF LIME CARBONATES IN SOILS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE in AGRONOMY

Cyril G. Hopkins
In Charge of Major Work

Cyril G. Hopkins
Head of Department

Recommendation concurred in:

Committee
on
Final Examination

246496

DURABILITY OF LIME CARBONATES IN SOILS.

INTRODUCTION.

Illinois has 28,048,323 acres[1] reported as improved agricultural land. There are between thirty and forty companies putting lime carbonates on the market for soil improvement. The Southern Illinois Penitentiary at Menard leads the list with an output in nineteen hundred and twelve of 21,475 tons. If all the plants had the same capacity as Menard there would be then less than a million tons per year. From the investigations[2] by the Illinois Experiment Station it would appear that at least half of the soils in this state or more, need liming and the present output would supply less than one-tenth of them with an application of one ton per acre per year. Even though the prices are reasonable (from 50 cents to $1.00 per ton[3] at the quarries in car load lots), and the output steadily increasing, there are still two other factors of vast importance, namely, distance from quarry and durability of the particular limestone used. The latter factor is the one that concerns this work.

In the northern part of this state are large deposits of almost chemically pure dolomite and since the knowledge concerning its action on soils is limited it was deemed necessary to make a special study of its durability and reaction with common Illinois soils. The present paper will be confined to a

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1. Thirteenth Census of U. S. 1910
2. Bul. 123, p. 196, and circ. 110. Ill. Expr. Sta.
3. Circ. 165, p. 18. Ill. Expr. Sta.

laboratory study of its durability as compared with calcium carbonate, magnesium carbonate and carbonate mixtures; in pure water, carbonated water, and in contact with soil.

HISTORICAL RESUME.

Over a century ago Sir Humphery Davy[1] told of the beneficial effect of magnesian limestones on peats and heavy soils.

Störer[2] in his book mentions the value of magnesium limes as ameliorants of heavy soils.

Von A. Atterberg[3] finds good effects on moor soils of Sweden by the application of dolomitic limestone. He also states that the injurious effects of magnesia were overcome by adding lime in the proportion existing in magnesian lime.

Dr. O. Kelner[4] states that some authorities report good effects from dolomite and some bad. Harmful effect was due to the leaching of lime and when sufficient lime was present, no harmful effect was noted.

D. Meyer[5] found in pot culture work with a mixed crop of grass and clover, that 5 grams of dolomite added to soil gave 24.9 grams of dried substance as compared to 23.9 with 2.5 grams of calcium oxide mixed 2.5 grams of magnesium oxide. Five grams of burned lime gave 22.85 grams of dried matter.

Frear[6] states that dolomites weather more slowly than

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[1] Sir Humphery Davy's Works. Vol. VIII. pp. 135-7.
[2] Störer's Agr. Chemistry. (1888) Vol. II. 135-7.
[3] Biedermanns Centr. Blatt. 21, (1892) pp. 298-9.
[4] Ldw. Vers. Stat. 47. pp. 208-10.
[5] Landw. Jahrb. 29 (1900), p.961.
[6] Penn. State Rept. 1899-1900. p.35.

pure limestones, owing to their more compact form. The specific gravity of dolomite is 2.8 to 2.95, while pure compact limestone is 2.6 to 2.8.

Dr. Stewart[1] gives the yields obtained on the Greenville farm in Utah which contains over forty per cent of the combined carbonates of calcium and magnesium in the first foot of soil. The magnesium carbonate constitutes about one-third.

EIGHT YEAR AVERAGE YIELD.

	Amt. of water applied.	Treatment	Aver. yield per acre.
Oats	15 in.	unmanured	82 bu.
Wheat	15 in.	"	50.4 bu.
Potatoes	20 in.	"	262.3 bu.
Sugar beets.	15 in.	manured	21.8 tons

Soils have been cropped for forty years and as far as known, fertilizer has never been applied. Manure was necessary to get a crop of sugar beets. In explanation of these results, Dr. Stewart states that the carbonates are most likely in the dolomitic form and the ratio of calcium to magnesium conforms to Loew's.

Dr. Wheeler[2] found, as a result of fifty-two field tests throughout the state of Rhode Island, with slacked lime, ground limestone, and dolomite, an increase in yield, no matter in what form the lime was applied.

Very little experimental field work has been reported to determine the effect of dolomite on soils, this is also true in regard to laboratory studies.

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[1] Jour. Ind. & Eng. Chem. Vol. III (1911) pp.376-8.
[2] Bul. 152. R.I. Expr. Sta.

T. S. Hunt[1] working with one gram of fine ground dolomite in one-half liter of water which was kept saturated with carbon dioxide at 18°C, found after eighteen hours .15 gram per liter of the combined carbonates was dissolved in proportion to fifty-seven parts of calcium carbonate and forty-three parts of magnesium carbonate. With two grams of dolomite and five days treatment the carbonated water dissolved .39 grams per liter.

In another paper Hunt[2] states that the insolubility of the double carbonate is an important fact in the history of dolomite.

Bischof[3] found by prolonged action of carbonated water on a limestone containing 11.54% magnesium carbonate, that 4.29% of the carbonate of lime dissolved and not a trace of magnesium. With a manganesian iron spar containing 15% magnesium carbonate and 14% calcium carbonate, four parts of calcium carbonate was dissolved to one part of magnesium carbonate in carbonated water.

Dr. Hartwell[4] found dolomite only one-third as soluble in saturated carbon dioxide water as calcium lime.

In carbonated water, Ferris[5] shows in three cases out of four that dolomite is only about half as soluble as the high calcium limestone. He[6] also gives the average amount of lime leached out per acre per annum for nine years as four hundred and thirty-eight pounds.

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1. Am. Jour. Sci. Vol. 42, (1866), p.52.
2. Ibid. Vol. 28, (1859) p.180.
3. Citation by Hunt. Am. Jour. Sci. Vol. 28,(1859), p.180.
4. Personal Communication to Dr. Whiting.
5. Studies in the Use of Lime and Limestones.Thesis, (1912) Uni. of Ill. p.10.
6. Ibid. p.35

Director A. D. Hall and Dr. Miller[1] report eight hundred pounds lost per acre per annum on Broadbalk Field as an average of forty years.

Reade[2] estimates the annual rainfall removes from the average square mile of the earth's surface, fifty tons of calcium carbonate and four tons of magnesium carbonate. On the acre basis this would amount to one hundred fifty-six pounds of calcium carbonate and twelve and one-half pounds of magnesium carbonate lost per acre per annum.

Thus vast quantities of calcium carbonate are leached from the soil every year and the problem before us is to find a substance that will perform the functions of calcium carbonate and endure longer. From the present knowledge dolomite is a very promising substitute.

EXPERIMENTAL.

This work is a continuation of the solubility studies commenced last year by Mr. Ferris. In the main the plan is to determine the solubility of dolomite in free and carbonated water, with and without soil. As a basis of comparison, the solubility of calcite, magnesite, precipitated calcium carbonate, precipitated magnesium carbonate, and various mixtures, was compared with the solubility of several dolomites. The following outline indicates the nature and extent of the work done.

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1. Proc. Roy. Soc. London. Vol. 77, (1905), p. 1-32.
2. Rock Weathering and Soils. Merrill. p.194.

Analysis of Carbonates Used.

A. Calcite. Obtained from Germany.
K. Limestone from Anna Deposit. Bag No.7.
8. Limestone.
3. Limestone. Kankakee, Ill.
C-1. Dolomite, Kankakee, Ill.
C-2. Dolomite, Chicago, Ill.
C-3. Dolomite, Thornton, Ill.
C-4. Magnesite, Porterville, Cal.

	A	K	8	3	C-1*	C-2*	C-3*	C-4*
$CaCO_3$	98.00	70.84	53.9	38.49	45.00	43.12	51.77	----
$MgCO_3$	-----	8.69	7.33	26.51	36.84	37.91	42.53	97.27

*Analysis reported on water free basis.

Analysis of Soils.

Brown Silt Loam (B.S.L.), Surface, Carlinville, Plot 301.

Light Gray Silt Loam (L.G.S.L.) Surface, Odin.

	B.S.L.	L.G.S.L.
Ca per Two million of Soil	7,000 ~~17,500~~	6,300 ~~15,750~~
Mg per Two million of Soil	4,220	4,495.

METHODS.

Distilled Water. One thousand cubic centimeters of boiling distilled water was placed in a liter Jena flask, stoppered and allowed to cool over night. Then made up to liter mark and sample added. The size of the sample varies with the material used, for soil one hundred grams; dolomite, calcite, and magnesite one gram and for the salt mixtures the equivalent of one gram of dolomite. With soil mixtures one gram of carbonate was added to one hundred of soil. The tightly stoppered flask was allowed to remain fifteen days with intermittent shaking and rapidly filtered. Temperature varied between eighteen to twenty degrees.

Carbonated Water. A carboy partly filled with distilled water was connected with two Kipp generators with a trap between to collect any hydrochloric acid that might be carried over with the carbon dioxide. Several days were required to thoroughly saturate a solution in this manner. Partial saturation could be obtained in a few hours. The strength of the carbonated water was determined by transferring one hundred cubic centimeters to an Erlenmeyer flask by means of a pipette and an excess of tenth normal barium hydroxide added, titrated back with tenth normal hydrochloric acid. When the water contained the desired saturation it was run into liter Jena flasks and the soil, soil mixtures, lime carbonates and carbonate mixtures added. Allowed to stand fifteen days with intermittent shaking and rapidly filtered.

Analytical Method. From four to seven hundred and fifty cubic centimeters of the filtered sample were subjected to analysis. Seven hundred and fifty cubic centimeters of the distilled water extract and five hundred of the carbonated water extract were the amounts generally used. Evaporate to dryness, take up with aqua regia, again run to dryness and again take up twice with hydrochloric acid. Add one cubic centimeter of ferric chloride and two-tenths of a gram of ammonium persulfate. Dilute to one hundred cubic centimeters, heat to boiling and precipitate with ammonium hydroxide. Filter and wash with hot water until free from chlorides. If the filtrate is colored the above procedure is repeated. Evaporate the clear ammoniated filtrate to one hundred cubic centimeters and add ten cubic centimeters of saturated ammonium oxalate. Allow to remain at sixty or seventy degrees for two hours, then filter and wash with hot water. Dissolve the washed precipitate in hot sulfuric acid solution (5 cc. of H_2SO_4 to 100 cc. H_2O) and titrate at sixty degrees against N/10 potassium permanganate.

The filtrate from the calcium oxalate was evaporated to seventy-five cubic centimeters, made neutral with hydrochloric acid and ten centimeters of microcosmic salt added, made slightly alkaline with ammonia and stirred vigorously until precipitate formed, allowed to stand thirty minutes, then added fifteen centimeters of ammonium hydroxide. Stood over night and the next morning washed with a three per cent solution of ammonia until freed from chlorides, then ignited. Weighed as magnesium pyrophosphate.

Note--Ammonium persulfate was used only when soil extracts were analyzed. Calcium carbonate in the soil solution possessed a stronger floculating action than the magnesium carbonate. This was noted in distilled water extract when the precipitated carbonates were used. According to Rohland[1] the hydroxide ion tends to deflocculate clay. The magnesium carbonate used contained some hydroxide.

RESULTS.

The results represent an average of two or more analyses unless otherwise stated. The solubilities are reported in every instance in milligrams per liter. From two to four grams of the carbonates were used with the carbonated water.

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[1] Citation by Bleininger. 8th Int. Cong. Appl'd Chem. Vol. 5,p.17.

Table I.

SOLUBILITY OF SOILS, CARBONATES, AND CARBONATE MIXTURES* IN DISTILLED WATER.

	Total mg. in solution per liter	Mg. of $CaCO_3$ per liter	Mg. of $MgCO_3$ per liter.
Precipitated $CaCO_3$	27.86	27.86	----
Calcite	15.99	15.99	----
Dolomite C-1	19.72	12.66	7.06
Dolomite C-2	19.12	12.66	6.46
Dolomite C-3	18.41	10.49	7.92
Precipitated $MgCO_3$	93.25	-----	93.25
Magnesite	16.56	-----	16.56
Brown silt loam	36.87	20.66	16.21
Light gray silt loam	20.85	10.66	10.19
Mixture of Prec. Carbonates	90.45	9.3	81.15
Mixture of Calcite and Magnesite	24.08	15.0	9.08

*The mixtures of the precipitated salts were in the ratio of dolomite C-1 while the calcite and magnesite had the ratio of dolomite C-3.

A significant feature in Table I is that dolomite, calcite, and magnesite have similar solubilities in distilled water, dolomite being slightly greater than the others. Mr. Ferris's(1)results show the same phenomenon. The mixture of the magnesite and calcite gave a higher solubility than the dolomite. The precipitated magnesium carbonate was about three and one-

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1. Studies and Use of Lime Carbonates. Thesis (1912) p.9.

half times as soluble in distilled water as the precipitated calcium carbonate. A mixture of the precipitated carbonates was slightly less soluble than the precipitated magnesium carbonate. The solubility of calcite approximates quite close to that given by Bineau[1], Schloesing and others.

Table II.

EFFECT DUE TO SOIL IN DISTILLED WATER EXTRACT.

	Brown Silt Loam Mgs. of CO_3 in solution per liter	Light Gray Silt Loam Mgs. of CO_3 in solution per liter	Effect of Brown Silt Loam	Effect of Light Gray Silt Loam
Precipitated $CaCO_3$	215.3	257.09	160.57	208.38
Calcite	155.14	143.71	102.28	106.87
Dolomite C-3	109.28	101.19	54.00	61.93
Precipitated $MgCO_3$	418.80	337.9	288.58	223.8
Magnesite	111.32	78.97	57.89	41.56
Mixture of Magnesite and calcite	158.36	149.90	97.41	52.47

Soil activity or effect was determined by adding the solubility of the soil alone to the carbonate alone and subtracting this result from the solubility of the mixture. The soils gave a positive reaction in distilled water. The light gray silt loam had a greater effect on the calcium than the brown silt loam, but a less effect on the magnesium. This is due probably to the light gray silt loam being more acid.

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1. Cited by Cameron. Bul. 49, p.39. Bureau of Soils.

Table III.

COMPARISON OF SOLUBILITIES.

A. In distilled water.

B. In carbonated water, 498.6 mgs. of CO_2 per liter.

C. In carbonated water, 846.4 mgs. of CO_2 per liter.

D. In carbonated water, 979. mgs. of CO_2 per liter.

	Total mgs. in solution	Total mgs. in solution Carbonated H_2O.	Total mgs. in solution	Total mgs. in solution.
	A	B	C	D
Dolomite C-1	19.72	150.7	----	154.93
" C-2	19.12	193.4	----	----
" C-3	18.41	-----	194.15	----
Calcite	15.99	-----	----	----
Magnesite	16.56	-----	----	----
Mixture of calcite and magnesite	24.08	-----	462.51	----
Precipitated $CaCO_3$	27.86	302.5	----	555.0
" $MgCO_3$	93.25	-----	----	----
Mixture of Precip. Carbonates	90.45	656.35	----	804.6
Brown Silt Loam	36.87	77.60	108.51	
Light Gray Silt Loam	20.85	38.49	43.70	----
B.S.L. + Dolomite C-3	109.28	-----	224.8	----
" + Calcite	155.14	-----	433.2	----
" + Magnesite	111.32	-----	189.84	----
" + Mix. of calcite and magnesite	158.36	-----	411.84	----
L.G.S.L. + Dolomite C-3	101.19	-----	166.1	----
" + Calcite	143.71	-----	332.61	----
" + Magnesite	78.97	-----	110.36	----
" + Mix. of calcite and magnesite	140.9	-----	339.14	----

Table IV.

SOLUBILITY IN CARBONATED WATER.

498.6 milligrams of carbon dioxide per liter.

	Total mgs. in solution	mgs. of $CaCO_3$ in solution	mgs. of $MgCO_3$ in solution	Effect of soil
Dolomite C-1	150.7	92.25	68.45	
Brown Silt Loam	77.60	50.75	26.85	
B.S.L. + Dolomite C-1	181.1	116.0	65.1	-47.2
Light Gray Silt Loam	38.49	25.0	13.49	
L.G.S.L. + Dol. C-1	112.1	65.0	47.1	-77.09
Dolomite C-2	193.4	103.0	90.4	
Mixture of Precip. $CaCO_3$ and $MgCO_3$	656.35	115.0	541.35	
B.S.L. + Precip. $CaCO_3$ and $MgCO_3$	492.9	157.5	335.4	
L.G.S.L. + Precip. $CaCO_3$ and $MgCO_3$	390.0	76.0	314.0	
Precipitated $CaCO_3$	302.5	302.5	-----	

Table V.

SOLUBILITY IN CARBONATED WATER.

846.4 milligrams of carbon dioxide per liter.

	Total mgs. in solution	Mgs. of $CaCO_3$ in solution	Mgs. of $MgCO_3$ in solution	Effect of soil.
Dolomite C-3	194.15	101.5	92.65	
B.S.L. + Dolomite C-3	224.8	133.0	91.8	-77.86
Brown Silt Loam	108.51	74.35	34.16	
L.G.S.L. + Dol. C-3	166.1	62.5	103.6	-71.75
Light Gray Silt Loam	43.7	30.5	13.2	
L.G.S.L. + Calcite	332.61	305.5	27.11	
" + Magnesite	110.36	41.0	69.36	
" + Mix. of calcite + magnesite	339.14	281.0	58.14	
B.S.L. + calcite	433.20	367.0	66.20	
" + magnesite	189.94	101.5	88.34	
" + Mix. of calcite + magnesite	411.84	332.0	79.84	

Table VI.

RATIOS OF SOLUBILITY OF CALCIUM AND MAGNESIUM IN SATURATED CO_2, H_2O.

	Total mgs. in solution	Mgs. of $CaCO_3$	Mgs. of $MgCO_3$
Precipitated $CaCO_3$	555.0	555.0	
Limestone K	372.3	360.7	11.61
Limestone 8	302.49	286.7	157.9
Precipitated $MgCO_3$	835.1	-----	835.1
Dolomite 3	144.18	89.7	64.48
Dolomite C-1	154.93	81.75	73.18
Dolomite C-3	194.15	101.5	92.65

Summary

Whenever the soil and carbonates were in contact in distilled water, the solubility of the latter was increased.

The results seem to show a depression when the soil was in contact with carbonates in carbonated water. The reason for this we cannot state at this time until more work is done.

The solubilities of the calcium and magnesium from the dolomites in the carbonated water existed in the same ratio as found in their respective dolomite. In all cases, dolomite was less active in soils than calcite and generally slightly more active than magnesite.

The work is still in progress and it is difficult to draw conclusions at this time.

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